

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C10M 135/10, 129/26, 129/92	A1	(11) International Publication Number: WO 96/35765 (43) International Publication Date: 14 November 1996 (14.11.96)
(21) International Application Number: PCT/US95/05783 (22) International Filing Date: 11 May 1995 (11.05.95) (71) Applicant (for all designated States except US): EXXON RESEARCH & ENGINEERING COMPANY [US/US]; 180 Park Avenue, P.O. Box 390, Florham Park, NJ 07932-0390 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): STADTMILLER, William, H. [US/US]; 47 Fordham Place, Colonia, NJ 07069 (US). (74) Agents: ALLOCCA, Joseph, J. et al.; Exxon Research and Engineering Company, P.O. Box 390, Florham Park, NJ 07932-0390 (US).		(81) Designated States: CA, US. Published <i>With international search report.</i>
(54) Title: LUBRICATING OIL (57) Abstract A composition and a method for reducing rust in machines using lubricating oils by employing a lubricating oil formulation comprising a major amount of a base oil stock having a viscosity in the ISO 10 to 1500 grades range and a minor amount of an additive comprising a metal synthetic alkylated aryl sulfonate and aliphatic substituted succinic anhydride or acid. The formulation exhibits a high level of rust inhibiting performance, while not adversely affecting any other desirable lubricating oil properties.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

LUBRICATING OIL

Field of the Invention

This invention relates to lubricating oils used in industrial machinery, e.g., hydraulic oil, gear oil, turbine oil, circulating oil, etc. and to the reduction of rust formation in such machinery.

Description of the Related Art

Many circulating and other industrial oils utilize natural (i.e., petroleum type) Group 2a metal sulfonates to impart detergency and rust protection characteristics.

However, it is often desirable to move to the synthetic metal sulfonates because the batch to batch characteristics of the synthetic types are more consistent/predictable since they do not depend on the variations found in the petroleum fractions utilized in manufacturing the natural sulfonates.

In the case of the natural alkaline earth Group 2a metal sulfonates, preferably barium and calcium, they provide excellent rust protection as measured by ASTM D665B (rust test).

In an attempt to move to lubricant formulations utilizing the more consistent quality and predictable Group 2a metal synthetic sulfonates it has been surprisingly found that the rust protection as measured by ASTM D665B test was directionally inferior to the protection provided by the corresponding natural sulfonates at approximately equivalent molar concentration (of metal from the sulfonate) (see Table 1, Runs 1, 2, 5, 6, 8, 9, 11, 12 and Table 4).

It was desirable, therefore, to determine how metal synthetic alkylated aryl sulfonates could be modified or combined with other materials in order to make them usable as predictable, high, consistent quality substitutes for the metal natural alkylated aryl sulfonates heretofore used as detergent and rust inhibiting additives in lubricating oil.

Summary of the Invention

It has been discovered that rust formation in industrial machinery employing a lubricating oil can be effectively reduced or arrested by using as the lubricating oil a formulation comprising a major portion of a base stock having a viscosity in the ISO 10 to 1500 viscosity grade range and a minor portion of an additive comprising a mixture of a metal salt of a synthetic alkylated aryl sulfonic acid (hereinafter metal synthetic alkyl aryl sulfonate) and an aliphatic substituted succinic acid or anhydride.

Detailed Description of the Invention

The present invention is directed to a composition and a method for reducing rust formation in industrial machinery using lubricating oils, e.g., hydraulic oil, gear oil, turbine oils, circulating oils, hereinafter lubricating oils, said method comprising lubricating the machinery with a lubricating oil composition comprising a major portion of a lubricating base oil stock having a viscosity in the ISO 10-1500 viscosity grade range and a minor portion of a rust resisting or reducing additive consisting of a mixture of a metal synthetic alkyl aryl sulfonate and an aliphatic substituted succinic acid or anhydride.

The circulating oil used in the present invention employs any natural or synthetic oil as base stock. The stock is selected from natural or synthetic stock having viscosities in the range 10 to 1500 cSt @ 40°C, preferably 32 to 680 cSt @ 40°C.

The natural base oils are the common petroleum derived stocks while the synthetic stocks include wax isomerate oils, poly alpha olefins, polyisobutylenes, alkyl-benzenes, polyol ester stocks including the products of mono- and di-carboxylic acids reacted with polyols and polyol ethers, silicone base oils, polyglycols, dibasic acid esters, alkyl and aryl phosphate esters, etc.

The base stock is employed as a single component or can be a combination of base stocks. The base oil of the formulation exhibits a final formulated oil viscosity in the ISO 10 to 1500 viscosity grade range, preferably ISO 32 to 680 viscosity grade range. Individual oils meeting this final viscosity requirement can be used as such as the base stock or a mixture of petroleum derived natural oils and/or synthetic oils of differ-

ing viscosities can be combined and blended to produce a mixed oil base stock meeting the final product target specification.

Additives are employed to bestow rust resistance, demulsibility, detergency, oxidation resistance, wear and extreme pressure resistance, friction modification, anti-foam protection, filterability and so forth to the oil and render it useful as an industrial machine oil. The additive imparting rust resistance to the formulation consists of a mixture of metal synthetic alkyl aryl sulfonates and aliphatic substituted succinic acid or anhydride.

The metal synthetic alkyl aryl sulfonate is used in an amount in the range 0.1 to 3 wt% based on the lubricating oil formulation, preferably 0.25 to 2 wt%, most preferably 0.25 to 1 wt% of the lubricating oil formulation while the aliphatic substituted succinic acid or anhydride is used in an amount in the range 0.01 to 2.0 wt% based on the lubricating oil formulation, preferably 0.02 to 0.2 wt%, most preferably 0.02 to 0.1 wt% of the circulating oil formulation.

The sulfonate component is identified as a metal synthetic alkyl aryl sulfonate. The metal is selected from the group consisting of Group 2a metals, Group 1a metals, transition metals such as zinc and mixtures thereof, preferably barium, calcium and mixtures thereof.

Synthetic alkyl aryl sulfonates are synthesized by procedures known to the arts, usually from benzene, toluene, xylene, ethylbenzene, cresol, naphthalene, anthracene or phenanthrene and mixtures thereof, preferably benzene or naphthalene as a starting material using particular carbon number alkyl oligomers as alkylating agents. In the present invention the alkylating agents used are propylene and butylene oligomers, preferably propylene oligomers of 9 to 30 carbons, more preferably 9 to 18 carbons, most preferably 12 to 15 carbons, and butylene/isobutylene oligomers of 8 to 20 carbons preferably 8 to 16 carbons, and result in the polyalkylation, usually dialkylation of the aromatic moiety. In cases of monoalkylation, the alkylating agent would be an oligomer of propylene and/or butylene of 12 to 30 carbons, preferably 16 to 27 carbons.

The alkylated aromatic is then sulfonated to the sulfonic acid. The sulfonic acids produced in the sulfonation reaction are converted to the respective sulfonates by reacting the sulfonic acids with a base. Suitable bases are the alkali metal hydroxides

(sodium, lithium, potassium) and alkaline earth hydroxide, carbonate, etc. (calcium, barium, magnesium), preferably the calcium or barium hydroxides or carbonates.

The synthetic alkyl aromatic sulfonates differ from the natural sulfonates by being synthesized using specific aromatics, and narrow carbon range number alkylating agents whereas the natural sulfonates use petroleum oil or white oil base as the source of aromatics and the alkyl side chains which introduces much greater variation in the type and carbon number of the alkyl groups.

Sulfonation can be classified as neutral, basic and overbased.

In the case of neutral sulfonates, essentially a stoichiometric amount of metal oxide or metal hydroxide is used to neutralize the sulfonic acid. Usually a very slight excess of base is employed to ensure complete reaction and leave the product just slightly on the basic side.

In the case of basic sulfonates an overtreat of hydroxide is used such that the hydroxide is not fully neutralized by the sulfonic acid.

Overbased sulfonates are produced by starting with a neutral or basic sulfonate and treating them with surfactants, lime or other metal base and CO₂ to yield a colloidal sol of suspended colloidal Metal carbonate which provides excess basicity. Overbased sulfonates are especially desirable in certain automotive and marine lubricant applications.

The metal synthetic alkyl aromatic sulfonates used in the industrial lubricants employed in the present invention are preferably barium or calcium synthetic alkyl benzene sulfonate, barium or calcium synthetic alkyl naphthalene sulfonate, most preferably barium or calcium didodecyl benzene sulfonate, barium or calcium dinonyl naphthalene sulfonate, and mixtures of such materials.

As previously indicated, the present invention is directed to a composition and a method for lubricating industrial machinery so as to reduce rust formation in such machinery while maintaining the other desirable properties needed to ensure adequate lubrication.

Industrial lubricating oils have traditionally employed natural alkyl aryl sulfonates of the neutral type as detergent and rust inhibitor additives. When synthetic dialkyl benzene sulfonate was tried, the oil surprisingly failed the rust inhibition test ASTM D665B (B indicates the test uses sea water). The ASTM D665B version is usually considered more severe than ASTM D665A (using distilled water) and is often a prerequisite for premium quality industrial lubricating oils.

The aliphatic substituted succinic acids or anhydrides are those materials bearing aliphatic groups containing from 20 to 200 carbons, preferably 20 to 100 carbons, most preferably 50 to 70 carbons, the aliphatic group, consequently being of from about 280 to 2800 molecular weight, most preferably about 700 to 1000 molecular weight wherein the aliphatic substituents are usually olefin homopolymers or copolymers, e.g., homopolymers or copolymers, of ethylene, propylene, butylene isobutylene, etc. Thus, a typical aliphatic substituted succinic acid or anhydride is polyisobutylene succinic acid or anhydride (PIBSA) wherein the polyisobutylene moiety ranges from about 280 to 2800 molecular weight, most preferably about 700 to 1000 molecular weight. It has been found that for the present invention to function as desired, the aliphatic substituted succinic acid or anhydride can not be further substituted, such as by being further substituted with alcohols (e.g., pentaerythritol) or amines such as polyamines. As used herein and in the claims, aliphatic substituted succinic acid or anhydride is understood to exclude such additionally substituted molecules as aliphatic substituted succinic acid or anhydrides condensed, reacted with or substituted with pentaerythritol (PE), polyamine (PAM), etc. Thus PIBSA-PAM or PIBSA-PE are not within the scope of the term aliphatic substituted succinic acid or anhydride.

Unexpectedly it has been found that metal synthetic alkyl aryl sulfonate combined with aliphatic substituted succinic acid or anhydride functions as an additive which imparts to circulating oil formulations good rust inhibition, as measured by ASTM D665B, while not adversely affecting other desirable lubrication properties.

The lubricating oils used in the lubrication process of the present invention may contain additional additives to impart particular functions and characteristics. Thus, anti-oxidants can be included in the formulation used. Anti-oxidants include sterically hindered phenols, such as tertiary butyl phenols, methyl ditertiary butyl phenol, 2,4,6 tri tertiary butyl phenols, 4,(N,N-dimethyl aminomethyl) 2,6-ditertiary butyl phenol,

ethyl di tertiary butyl phenol and their homologs and analogs. Methylene bridged alkyl phenols can also be used, either alone or in combination with the aforesaid sterically hindered phenols. Representative hindered methylene bridged phenolic compounds are 4,4¹ methylene bis (6 tert butyl-o-cresol), 4,4¹ methylenebis (2-tert amyl-o-cresol) and similar compounds. See USP 3,211,632. 3,5 ditertiary butyl-4 hydroxy hydro cinnamic acid esters are also suitable hindered phenols. Oil soluble secondary aromatic amine compounds may also be used as anti-oxidants, such compounds include diphenylamine, alkyl diphenylamine containing one or two alkyl substituents each having up to 16 carbon atoms, phenyl α naphthylamine, phenyl β naphthylamine, alkyl or aralkyl substituted phenyl α/β naphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbons, NN dialkyl O-phenylenediamine and similar compounds. Anti-oxidants may be used in amounts in the range up to 5 wt% preferably less than 2 wt%. Demulsifiers can also be included in the circulating oil. Demulsifiers are liquid nonionic surface active agents such as amine glycol condensates. Other materials include polyethylene oxides, polypropylene oxides, block copolymers of ethylene oxide and propylene oxide, salt and esters or oil soluble acids and the like. Oxyalkylated alkylphenol-formaldehyde condensates can also be used as demulsifiers. These materials typically have molecular weight in the range 4000 to about 6000. Polyoxyalkylene glycols and oxyalkylated alkylphenolic resins are also suitable for use as demulsifiers. Demulsifiers may be used in amounts in the range 0.001 to 0.2 wt%. Anti wear/extreme pressure/friction modifiers can also be used and these include metal dialkyl dithiophosphates, metal diaryldithiophosphates, aryl phosphates, alkylaryl phosphates, (e.g., tricresylphosphate, triarylphosphate), phosphorized fats and olefins, sulfurized fats and olefins. Anti wear/extreme pressure/friction modifiers may be used in amounts in the range up to 5 wt% preferably about 0.2 to 2 wt%. Corrosion inhibitors can be added such as the various triazoles, e.g., benzotriazole, tolyltriazole and alkyl substituted benzotriazole, the alkyl substituents containing up to 15 carbons, derivatives of triazoles and benzotriazoles and substituted materials such as dimercaptotriazole bis alkyl disulfide. Corrosion inhibitors are used typically at concentrations of less than 2 wt%, preferably less than 0.5 wt%.

Anti-foaming agents such as silicone oils, polysiloxanes, polyacrylates may be used, at concentrations in the range up to 0.2 wt%. Similarly, pour point depressants such as polyacrylates, polymethacrylates, chlorinated polymers, chlorinated wax, alkylated phenol polymers, polyesters and the like can be used, usually at concentrations in the range of 0.05 to 1.0 wt%.

Additives are generally described in "Lubricants and Related Products" by Dieter Klamann, Verlag Chemie, Deerfield Beach, Florida, 1984.

In general, these other additives can be used in lubricating industrial oils in total amounts in the range of 0.5 to 6 wt%, preferably 1.0 to 3 wt%.

Example 1

A series of industrial lubricating oils of ISO viscosity grade 220 was formulated using a variety of metal synthetic alkyl aryl sulfonates (neutral type sulfonates), aliphatic substituted succinic acid/anhydrides, substituted aliphatic substituted succinic acids/anhydrides and certain combinations thereof and evaluated for rust performance using ASTM D665B test. The results are presented in Table 1.

From these runs it is seen that using the metal synthetic alkyl aryl-sulfonates by themselves does not result in an oil which demonstrates good rust inhibition. Similarly using PIBSA by itself does not result in an oil with good rust resistance properties. The combination of metal synthetic alkyl aryl sulfonate and PIBSA is needed if the oil is to demonstrate good rust resistance properties. The runs also demonstrate that the use of substituted PIBSA, e.g., PIBSA-PAM, PIBSA-PE, does not result in oils exhibiting good rust resistance. More importantly, however, it is seen that such substituted PIBSA materials cannot be used in place of unsubstituted PIBSA in combination with the metal alkyl arylsulfonate. Combinations of metal synthetic alkyl aryl sulfonate and such substituted PIBSA materials produce oils which do not exhibit good rust resistance performance. Consequently such substituted materials cannot be used in the present invention and do not form part of the present invention.

TABLE 1

Additive Component (wt%)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Calcium didodecylbenzene sulfonate (1)	0.50	1.00	-	0.50	-	-	-	-	-	-
Barium didodecylbenzene sulfonate (2)	-	-	-	-	0.53	1.10	0.53	-	-	-
Barium dinonyl naphthalene sulfonate (3)	-	-	-	-	-	-	-	0.51	1.03	0.51
Calcium dinonyl naphthalene sulfonate (4)	-	-	-	-	-	-	-	-	-	-
Polyisobutylenesuccinic acid or anhydride (PIBSA) [950 MW PIB] (5)	-	-	0.08	0.04	-	-	0.04	-	-	0.04
PIBSA-PAM [PIB 950 MW] (6)	-	-	-	-	-	-	-	-	-	-
PIBSA-PAM [PIB 950 MW] (7)	-	-	-	-	-	-	-	-	-	-
PIBSA-PE [PIB 900 MW] (8)	-	-	-	-	-	-	-	-	-	-
PIBSA-PAM [PIB 2225 MW] (9)	-	-	-	-	-	-	-	-	-	-
Result: ASTM D665B Rust Test	Fail	Fail	Fail	Pass	Fail	Fail	Pass	Fail	Fail	Pass
approximate ppm metal from sulfonate	100	200	-	100	343	686	343	343	686	343
100 ppm Ca is equivalent to about 343 ppm Ba										
200 ppm Ca is equivalent to about 686 ppm Ba										

TABLE 1 (continued)

Additive Component (wt%)	Run 11	Run 12	Run 13	Run 14	Run 15	Run 16	Run 17	Run 18	Run 19	Run 20	Run 21
Calcium didodecyl benzene sulfonate (1)	-	-	-	-	0.50	-	0.50	-	0.50	-	0.50
Barium didodecylbenzene sulfonate (2)	-	-	-	-	-	-	-	-	-	-	-
Barium dinonyl naphthalene sulfonate (3)	-	-	-	-	-	-	-	-	-	-	-
Calcium dinonyl naphthalene sulfonate (4)	0.50	1.0	0.50	-	-	-	-	-	-	-	-
PIBSA (950 MW PIB) (5)	-	-	0.04	-	-	-	-	-	-	-	-
PIBSA-PAM [PIB 950 MW] (6)	-	-	-	.13	0.064	-	-	-	-	-	-
PIBSA-PAM [PIB 950MW] (7)	-	-	-	-	-	0.13	0.064	-	-	-	-
PIBSA-PE [PIB 900 MW] (8)	-	-	-	-	-	-	-	0.13	0.064	-	-
PIBSA-PAM [PIB 2225MW] (9)	-	-	-	-	-	-	-	-	-	0.28	0.14
Result: ASTM D665B Rust Test	Fail	Fail	Pass	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail
approximate ppm metal from sulfonate	100	200	100	-	100	-	100	-	100	-	100
100 ppm Ca is equivalent to about 343 ppm Ba											
200 ppm Ca is equivalent to about 686 ppm Ba											

- 10 -

- (1) Calcium didodecylbenzene sulfonate, neutral type; MW ~1026 as the Ca sulfonate; Active ingredient approximately 55%.
- (2) Barium didodecylbenzene sulfonate, neutral type; MW ~1123 as the Ba sulfonate; Active ingredient approximately 60%.
- (3) Barium dinonylnaphthalene sulfonate, neutral type; MW ~1055; Active ingredient approximately 50%.
- (4) Calcium dinonylnaphthalene sulfonate, neutral type; MW ~958; Active ingredient approximately 50%.
- (5) Polyisobutylene succinic anhydride (or acid) PIBSA derived from polyisobutylene of approximately 950 MW. This PIBSA product has approximately a saponification number of 112, and an active ingredient content of approximately 72% after discounting for oil diluent and unreacted polyisobutylene.
- (6) Reaction product of PIBSA (described above) and polyethylene amine (PAM). This PIBSA-PAM product is approximately 50% active ingredient and the ratio of PIBSA/PAM is approximately 2.2; the product has a nitrogen content of approximately 1.58 mass %.
- (7) Reaction product of PIBSA, described above, and polyethylene amine (PAM). This PIBSA-PAM product is approximately 50% active ingredient and the ratio of PIBSA/PAM is approximately 1.5; the product has a nitrogen content of approximately 2.13 mass %.
- (8) Reaction product of PIBSA of approximately 900 MW polyisobutylene and a polyol, pentaerythritol (PE). This PIBSA-PE product is believed to be approximately 50% active ingredient.
- (9) Reaction product of PIBSA (derived from polyisobutylene of approximately 2225 MW) and polyethylene amine (PAM). This PIBSA-PAM product is approximately 45% active ingredient and the ratio of PIBSA/PAM is approximately 2.0; the product has a nitrogen content of approximately 0.9 mass %.

Example 2

A series of industrial lubricating oil of ISO viscosity grades 32, 68, 100, 150, and 460 was formulated using calcium didodecyl benzene sulfonate and a PIBSA (950 MW PIB described in Example 1, Footnote 5) and evaluated for rust performance using ASTM D 665B test. All calcium concentrations are approximately 100 ppm. The results are presented in Table 2.

From this it is seen that the rust inhibiting effect of using the combination of metal synthetic alkyl aryl sulfonate and alkyl substituted succinic acid/anhydride is relatively uniformly effective across the ISO viscosity grades and is not a function of the molecular weight (viscosity) of the base oil utilized.

TABLE 2

ISO Viscosity Grade	32	32	32	32	68	68	68	68
Additive Component (wt%)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
Calcium didodecylbenzene sulfonate (1)	0.5	1.00	-	0.50	0.50	1.00	-	0.50
Polyisobutylenesuccinic acid or anhydride (950 MW PIB) (5)	-	-	0.08	0.04	-	-	0.08	0.04
Test Results - Rust Test ASTM D665B	Fail	Fail	Fail	Pass	Fail	Fail	Fail	Pass

TABLE 2 (continued)

ISO Viscosity Grade	100	100	100	100	150	150	150	150	460	460	460	460
Additive Component (wt%)	Run	Run	Run	Run	Run	Run	Run	Run	Run	Run	Run	Run
Calcium didodecyl benzene sulfonate (1)	9	10	11	12	13	14	15	16	17	18	19	20
	0.50	1.00	-	0.50	0.50	1.00	-	0.50	0.50	1.00	-	0.50
Polyisobutylenesuccinic acid or anhydride (950 MW PIB) (5)	-	-	0.08	0.04	-	-	0.08	0.04	-	-	0.08	0.04
Test Results - Rust Test ASTM D665B	Fail	Fail	Fail	Pass	Fail	Fail	Fail	Pass	Fail	Fail	Fail	Pass

(1) see footnote 1 of Table 1 of Example 1.

(5) see footnote 5 of Table 1 of Example 1.

Example 3

A series of industrial lubricating oils of ISO viscosity grade 220 was formulated using different calcium synthetic alkyl benzene sulfonates and varying concentrations of the PIBSA component described in Examples 1 and 2 (footnote 5) and evaluated for rust performance using ASTM D665B test. The results are presented in Table 3. This shows that metal synthetic alkyl aryl sulfonates produced by different manufacturers behave in a similar fashion, that the effective concentration range of PIBSA is about 0.02 to 0.1% and higher and that the use of PIBSA alone does not enable the oil to pass the ASTM D665B test.

TABLE 3

Additive Component (wt%)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 13	Run 8	Run 9	Run 10
Calcium didodecylbenzene sulfonate (A)	0.50	0.50	0.50	0.50	0.50	0.50	-	-	-	-	-
Calcium didodecylbenzene sulfonate (B)	-	-	-	-	-	-	-	-	-	-	-
Calcium didodecylbenzene sulfonate (C)	-	-	-	-	-	-	-	-	-	-	-
Polyisobutylenesuccinic anhydride/acid (950 MW PIB)	-	0.10	0.05	0.025	0.012	0.006	0.1	0.08	0.05	0.025	0.012
Test Results - Rust Test ASTM D665B	Fail	Pass	Pass	Border-line Pass	Fail	Fail	Fail	Fail	Fail	Fail	Fail
approximate ppm metal from sulfonate	100	100	100	100	100	100	-	-	-	-	-

TABLE 3 (continued)

	Run 11	Run 12*	Run 14	Run 15	Run 16	Run 17	Run 18	Run 19
Additive Component (wt%)								
Calcium didodecylbenzene sulfonate (A)	-	-	-	-	-	-	-	-
Calcium didodecylbenzene sulfonate (B)	-	-	1.0	0.50	0.50	-	-	-
Calcium didodecylbenzene sulfonate (C)	-	-	-	-	-	1.0	0.50	0.50
Polvisobutylene succinic anhydride/acid (950 MW PIB)	0.006	-	-	-	0.04	-	-	0.04
Test Results - Rust Test ASTM D665B	Fail	Fail	Fail	Fail	Pass	Fail	Fail	Pass
approximate ppm metal from sulfonate	-	-	200	100	100	200	100	100

- (A) Calcium didodecylbenzene sulfonate described in Examples 1 and 2, Tables 1 and 2 [footnote 1].
 (B) A product by a different manufacturer also identified as the neutral calcium didodecylbenzene sulfonate.
 (C) A product by a different manufacturer believed to be the neutral calcium didodecylbenzene sulfonate.
 (*) Contains ISO 220 viscosity grade base oil only.

Example 4

A series of industrial lubricating oils of ISO viscosity grade 46 and 220 was formulated using natural neutral type calcium sulfonate and natural barium sulfonate and evaluated for rust performance using ASTM D665B test. The results are presented in Table 4, below:

TABLE 4

ISO Viscosity Grade	220				46	
Additive Component (wt %)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Natural calcium sulfonate (1)	.57	.285	-	-	.57	-
Natural barium sulfonate (2)	-	-	.93	.465	-	.93
Test result - Rust Test ASTM D 665 B	Pass	Pass	Pass	Pass	Pass	Pass
approximate ppm metal from sulfonate	100	50	343	172	100	343

- (1) Natural calcium sulfonate, neutral type. Molecular weight is approximately 1140.
- (2) Natural barium sulfonate, neutral type. Molecular weight is approximately 1240.

The test shows that the natural metal sulfonates give excellent rust protection to the lubricating oil at relatively low concentrations and can be used for that purpose without additional additive.

CLAIM:

1. A lubricating oil composition comprising a lubricating oil basestock and a rust resisting or reducing additive consisting of mixtures of a metal synthetic alkyl aryl sulfonate present in an amount in the range of 0.1 to 3 wt% based on the lubricating oil and an aliphatic substituted succinic acid or anhydride present in an amount in the range 0.01 to 2.0 wt% based on the lubricating oil.
2. The lubricating oil of claim 1 wherein the lubricating oil base stock has a viscosity in the ISO 10 to 1500 viscosity grade range.
3. The lubricating oil of claim 1 or 2 wherein the metal synthetic alkyl aryl sulfonate is present in an amount in the range 0.25 to 2 wt% and the aliphatic substituted succinic acid or anhydride is present in an amount in the range 0.02 to 0.2 wt%.
4. The lubricating oil of claim 1 or 2 wherein the metal of the metal synthetic alkyl aryl sulfonate is selected from the group consisting of calcium, barium and mixtures thereof.
5. The lubricating oil of claim 1 or 2 wherein the metal synthetic alkyl aryl sulfonate is selected from the group consisting of neutral barium or calcium di-dodecyl benzene sulfonate, neutral barium or calcium dinonyl naphthalene sulfonate and mixtures thereof.
6. The lubricating oil of claim 1 or 2 wherein the aliphatic substituent in the succinic acid or anhydride has a molecular weight in the range 280 to 2800.
7. The lubricating oil of claim 1 or 2 wherein the aliphatic substituent in the succinic acid or anhydride has a molecular weight in the range 700 to 1000.
8. A method for reducing or preventing rust formation in machinery by lubricating the machinery using a lubricating oil comprising a lubricating oil base stock and a rust resisting or reducing additive consisting of a mixture of a metal synthetic alkyl aryl sulfonate present in an amount in the range 0.1 to 3 wt% based on

the lubricating oil and an aliphatic substituted succinic acid or anhydride present in an amount in the range 0.01 to 2.0 wt% based on the lubricating oil.

9. The method of claim 8 wherein the lubricating oil base stock has a viscosity in the ISO 10 to 1500 viscosity range.

10. The method of claim 8 or 9 wherein the metal synthetic alkyl aryl sulfonate is present in an amount in the range 0.25 to 2 wt% and the aliphatic substituted succinic acid or anhydride is present in an amount in the range 0.02 to 0.2 wt%.

11. The method of claim 8 or 9 wherein the metal of the metal synthetic alkyl aryl sulfonate is selected from the group consisting of barium, calcium and mixtures thereof.

12. The method of claim 8 or 9 wherein the metal synthetic alkyl aryl sulfonate is selected from the group consisting of neutral barium or calcium didodecyl benzene sulfonate, neutral barium or calcium dinonyl naphthalene sulfonate and mixtures thereof.

13. The method of claim 8 or 9 wherein the aliphatic substituent in the succinic acid or anhydride has a molecular weight in the range 280 to 2800.

14. The method of claim 8 or 9 wherein the aliphatic substituent in the succinic acid or anhydride has a molecular weight in the range 700 to 1000.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/05783

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10M 135/10, 129/26, 129/92

US CL : 252/33, 33.2, 56D

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/33, 33.2, 56D

and IPC(6) C10M 135/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,023,016 (GALLACHER ET AL) 11 June 1991, col. 2, lines 35-61.	1-14
Y	US, A, 3,288,714 (OSUCH) 29 November 1966, col. 1, lines 13-47 and col. 3, lines 43-51.	1-14
Y	US, A, 3,030,387 (BENOIT, JR.) 17 April 1962, col. 1, lines 16-35.	1-14
A	US, A, 5,221,490 (TAJIRI ET AL) 22 June 1993, col. 2, lines 62-66	1-14
A	US, A, 4,759,861 (OGURA ET AL) 26 July 1988, col. 2, lines 27-42.	1-14
A	US, A, 4,159,958 (de VRIES) 03 July 1979, col. 1, lines 26-36.	1-14

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A document defining the general state of the art which is not considered to be of particular relevance	*X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E earlier document published on or after the international filing date	*Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z document member of the same patent family
*O document referring to an oral disclosure, use, exhibition or other means	
*P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

19 JUNE 1995

Date of mailing of the international search report

07 AUG 1995

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer
ELLEN MCAVOY

Telephone No. (703) 305-2510

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/05783

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,509,052 (MURPHY) 28 April 1970, col. 2, lines 13-21.	1-14

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*

THIS PAGE BLANK (USPTO)